Statistical Thermodynamics in Chemistry and Biology

11. The statistical mechanics of simple gases and solids

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Partition functions for atoms and molecules

Today's agenda

▶ Derive expressions for the molecular partition function:

  ▶ Translation
  ▶ Rotation
  ▶ Vibration
  ▶ Electronic excitations

Quantum mechanics, summary

▶ The states of atoms and molecules are described by quantum mechanics.

▶ The energy is quantized and light and matter interact: $\Delta E = h\nu$.

▶ The fundamental equation is the Schrödinger equation: $\hat{H}\psi_i = E_i\psi_i$.

▶ The Hamiltonian, $\hat{H}$, is an operator and consists of a kinetic energy operator, $\hat{K}$, and a potential energy operator, $\hat{V}$,

$$\hat{H} = \hat{K} + \hat{V}$$

▶ The Schrödinger equation can only be solved exactly for a handful of model systems because of the complexity of the potential energy.

Quantum mechanics

The Schrödinger equation

▶ Eigenvalue problem:

$$\hat{H}\psi_i = E_i\psi_i$$

where $\hat{H}$ is the Hamilton operator, ψ_i is the wavefunction (eigenfunction), and E_i is the energy (eigenvalue).

▶ The energy is quantized, which is denoted by that a quantum mechanical particle is in a state i.

▶ If several states have the same energy, they are said to be degenerate.

Quantum mechanics

The Hamilton operator

▶ The Hamiltonian is the energy operator,

$$\hat{H} = \hat{K} + \hat{V}$$

and consists of a kinetic energy operator, $\hat{K}$ and a potential energy operator, $\hat{V}$.

▶ For N particles, the kinetic energy is always the sum of the particle kinetic energies,

$$\hat{K} = \sum_i^N \frac{\hat{p}_i^2}{2m_i}$$

▶ The potential energy is unique for each type of system. For a molecule, it is the Coulomb interaction between all the particles:

$$\hat{V} = \sum_{i,j>i}^N \frac{q_i q_j}{4\pi\varepsilon_0 \hat{R}_{IJ}}$$

Quantum mechanics
Separation of variables

▶ If the Hamiltonian can be separated into a sum of the form,

$$\hat{H}(x, y, z) = \hat{H}_1(x) + \hat{H}_2(y) + \hat{H}_3(z)$$

then we can do a variable separation into separate problems, e.g.,

$$\hat{H}_1 \psi_i^{(1)}(x) = E_i^{(1)} \psi_i^{(1)}(x); \ \hat{H}_2 \psi_j^{(2)}(y) = E_j^{(2)} \psi_j^{(2)}(y); \ \hat{H}_3 \psi_k^{(3)}(z) = E_k^{(3)} \psi_k^{(3)}(z)$$

▶ The total energy becomes the sum of the different contributions,

$$E_{i,j,k} = E_i^{(1)} + E_j^{(2)} + E_k^{(3)}$$

and the total wavefunction becomes the product,

$$\psi_{i,j,k}(x, y, z) = \psi_i^{(1)}(x)\psi_j^{(2)}(y)\psi_k^{(3)}(z)$$

Quantum mechanics
The Born-Oppenheimer approximation

▶ The molecular wavefunction is separated into two parts, one for the electrons and one for the nuclei:

$$E_m = E_i + E_n$$

▶ The nuclear part is further divided into translation (of the entire molecule), rotation (of the entire molecule) and vibrations (internal motion in the molecule),

$$E_n = E_j + E_k + E_l$$

▶ It takes 3 coordinates (degrees of freedom) to describe the translational motion of the molecule, 3 coordinates (degrees of freedoms) to describe rotation of the entire molecule. Thus, we have $3N - 6$ vibrational degrees of freedoms (linear molecules is an exception).

Model systems in quantum mechanics

- ▶ Particle-in-a-box (model for translation)
- ▶ Harmonic oscillator (model for vibration)
- ▶ Rigid rotor (model for rotation)

Particle-in-a-box

▶ One-dimensional problem: $\hat{V} = 0$ in $0 \leq x \leq L$, otherwise $\hat{V} = \infty$.

$$\varepsilon_n = \frac{(nh)^2}{8mL^2}, \quad n = 1, 2, 3, \ldots$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

▶ Calculate the partition function, q_t:

$$q_t = \sum_{n=1}^{\infty} e^{-\frac{\varepsilon_n}{k_B T}} = \sum_{n=1}^{\infty} e^{-\frac{n^2 h^2}{8mL^2 k_B T}}$$

▶ Define the translational temperature, θ_t as

$$\theta_t = \frac{h^2}{8mL^2 k_B} \qquad \Rightarrow \qquad q_t = \sum_{n=1}^{\infty} e^{-\frac{n^2 \theta_t}{T}}$$

Particle-in-a-box
Part 2

▶ In most cases $\theta_t \ll T$, which means that the energy spacings are small. Thus approximate as an integral

$$q_t = \int\limits_{0}^{\infty} e^{-\frac{h^2 n^2}{8mL^2 k_B T}} \, dn = \sqrt{\frac{2\pi m k_B T}{h^2}} L$$

where we have used a standard integral in Appendix K.

▶ Generalize to three dimensions. Separation of variables gives

$$\varepsilon_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

where a, b and c, are the dimensions of the box.

▶ Exercise: For which combinations of values of a, b, and c, do we get degenerate states? *Two of a, b or c are identical*

Particle-in-a-box
Part 3

▶ The partition function in three dimensions,

$$q_t = q_x q_y q_z = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} abc = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V$$

where V is the volume of the box.

▶ Sometimes we introduce Λ (a characteristic length) as

$$\Lambda^3 = \left(\frac{h^2}{2\pi m k_B T}\right)^{\frac{3}{2}}$$

such that

$$q_t = \frac{V}{\Lambda^3}$$

Harmonic oscillator

▶ The vibrations in a molecule is approximated by a Harmonic oscillator.

▶ The potential energy as a function of an internal coordinate (e.g. bond length) is often approximated with a Taylor expansion:
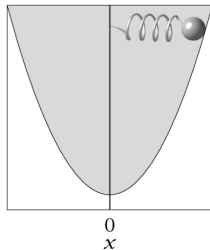
$$V(x) = V(0) + xV^{(1)}(0) + \frac{1}{2}x^2 V^{(2)}(0) + \frac{1}{6}x^3 V^{(3)}(0) + \ldots$$

$\mathcal{V}(x) = k_s x^2 / 2$

0

x

▶ $V(0)$ only shifts the zero level; the gradient is 0 at the minimum; the anharmonicity, $V^{(3)}(0)$ and higher order terms may be neglected in a first approximation:

$$V(x) = \frac{1}{2}x^2 V^{(2)}(0) = \frac{1}{2}k_s x^2$$

where k_s is the force constant.

Harmonic oscillator
Part 2

▶ The solutions for the Schrödinger equation:
   ▶ The energy levels are given as

$$\varepsilon_n = \left(n + \frac{1}{2} \right) h\nu \ , \ \ n = 0, 1, 2, \ldots$$

   where the frequency ν is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_s}{\mu}}$$

   and the *reduced mass*, μ, is given for a diatomic molecule as

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

   ▶ We have a zero-point vibrational energy: $\varepsilon_0 = \frac{1}{2} h\nu$
   ▶ The wave function is given in terms of *Hermite polynomials*
▶ Alternative expressions: $h\nu = \frac{hc}{\lambda} = \hbar\omega$, where $\hbar = h/2\pi$.

Harmonic oscillator

Part 3: as it was done in the 1st ed. of the book

▶ The molecular partition function for vibrations, q_v,

$$q_V = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)h\nu} = e^{-\frac{\beta h\nu}{2}} \left(1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + e^{-3\beta h\nu} + \dots\right)$$

$$= e^{-\frac{\beta h\nu}{2}} \left(1 + x + x^2 + x^3 + \dots\right) \quad \text{for } x = -\beta h\nu$$

▶ Use the series expansion (Appendix J.6, $p = 1$, $x \to -x$),

$$(1 - x)^{-1} = 1 + x + x^2 + x^3 + \dots, \quad |x| < 1$$

▶ Thus the partition function becomes

$$q_v = \frac{e^{-\frac{\beta h\nu}{2}}}{1 - e^{-\beta h\nu}}$$

Harmonic oscillator
Part 4: as it is done in the 2nd ed. of the book

▶ We ignore the zero-point vibrational energy,

$$\varepsilon_n \approx nh\nu$$

▶ The partition function becomes, in analogy to the previous slide,

$$q_v \approx \sum_{n=0}^{\infty} e^{-\beta nh\nu} = \left(1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \dots\right) = \frac{1}{1 - e^{-\beta h\nu}}$$

which is the expression used in most text books.

Rigid rotor model

- ▶ The rigid rotor is used to describe rotation of molecules.
- ▶ The solution to the Schrödinger equation:
    - ▶ $\psi_{l,m}(\theta, \phi)$ depends on two quantum numbers, l and m
    - ▶ $l = 0, 1, 2, \ldots$, and $m = -l, -l+1, \ldots, 0, \ldots, l-1, l$
    - ▶ The energy is

$$\varepsilon_l = \frac{l(l+1)h^2}{8\pi I_m}$$

    where I_m is the moment of inertia.

$$I_m = \sum_i^N m_i R_i^2$$

    - ▶ The energy does not depend on the quantum number, m, i.e. the energy is degenerate with the degeneracy factor,

$$g(l) = 2l + 1$$

Rigid rotor model
Part 2

▶ The rotational partition function for a single particle, q_r,

$$q_r = \sum_{l=0}^{\infty} (2l + 1) \, e^{-\beta \varepsilon_l}$$

▶ For large temperatures, $T \gg \theta_r = \frac{\varepsilon_l}{k_B}$, q_r is approximated with an integral as

$$q_r = \frac{T}{\sigma \theta_r} = \frac{8\pi^2 I_m k_B T}{\sigma h^2}$$

where σ is a symmetry factor that accounts for the number of equivalent orientations.

$\sigma = 1$ heteronuclear diatomic molecules (e.g. HF, CO)
$\sigma = 2$ homonuclear diatomic molecule (e.g. N_2), but also water (H_2O)
$\sigma = 12$ methane (CH_4)

Electronic partition functions

▶ In general,

$$q_e = g_0 + g_1 e^{-\beta \Delta \varepsilon_1} + g_2 e^{-\beta \Delta \varepsilon_2} + \dots$$

where g_i is a degeneracy factor and $\Delta \varepsilon_i$ is an electronic excitation energy.

▶ Normally, electronic excitations only by interaction with light (no temperature equilibration) since $\frac{\Delta \varepsilon_1}{k_B} \approx 10000 - 100000 \, K$.

▶ In most cases, $g_0 = 1$

▶ Thus, normally

$$q_e = 1$$

The molecular partition function

▶ The translational, vibrational, rotational, and electronic energies are to a good approximation additive.

▶ Thus the molecular partition function, q, is given as

$$q = q_t q_v q_r q_e$$

▶ Note that

$$\ln q = \ln q_t + \ln q_v + \ln q_r + \ln q_e$$

▶ Also note that it is only q_t that depends on the volume, V, whereas q_t, q_v and q_r depends on the temperature, T.

▶ Also note that the dependence on the number of particles, N, enters in the total partition function, $Q = \frac{q^N}{N!}$, i.e. the partition function for a single molecule, q, is independent of N.

Ideal gas properties from quantum mechanics

Helmholtz free energy and pressure

▶ Ideal gas (noninteracting particles): $Q = \frac{q^N}{N!}$ for indistinguishable particles.

▶ Helmholtz free energy, F,

$$F = -k_B T \ln Q = -k_B T \ln \frac{q^N}{N!} = -Nk_B T \ln q + k_B T \ln N!$$

▶ It is noted that the molecular partition function can be written as $q = q_0 V$, (and thus $\ln q = \ln q_0 + \ln V$) since only the translational part depends on the volume.

▶ Pressure, p,

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = Nk_B T \frac{\partial \ln V}{\partial V} = \frac{Nk_B T}{V}$$

Ideal gas properties from quantum mechanics
Internal energy

▶ The internal energy, U, is given as (Eq. 10.34)

$$U = Nk_B T^2 \frac{\partial \ln q}{\partial T}$$

▶ For translational motion, $q_t = c_0 T^{\frac{3}{2}}$,

$$U = \frac{Nk_B T^2}{q} \frac{\partial q}{\partial T} = \frac{Nk_B T^2}{c_0 T^{\frac{3}{2}}} \frac{3}{2} c_0 T^{\frac{1}{2}} = \frac{3}{2} Nk_B T$$

▶ Similarly, for rotational motion, $q_r = c_1 T^{\frac{3}{2}}$,

$$U = \frac{3}{2} Nk_B T$$

▶ Each translational and rotational degree of freedom gives $\frac{1}{2} Nk_B T$.

▶ For *weak* vibrational modes ($q \gg 1$), gives a contribution $k_B T$ for each mode.

Ideal gas properties from quantum mechanics
Entropy

▶ Absolute entropies (in contrast to entropy differences) gives a fundamental validation of the indistinguishability of gas molecules.

▶ For a monoatomic gas, only the translational motion contributes. Using Stirling's approximation,

$$S = k_B \ln \frac{q^N}{N!} + \frac{U}{T} \approx N k_B \ln q - k_B \left(N \ln N - N \right) + \frac{3}{2} N k_B$$

$$= N k_B \left(\ln q - \ln N + \frac{5}{2} \right) = N k_B \ln \frac{q e^{\frac{5}{2}}}{N} = N k_B \ln \left(\left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \frac{e^{\frac{5}{2}}}{N} V \right)$$

which is the Sackur-Tetrode equation.

Ideal gas properties from quantum mechanics
Chemical potential

▶ The chemical potential will be the focus in Ch. 13-16.

▶ First rewrite the Helmholtz free energy using Stirling's approximation,

$$F = -k_B T \ln \frac{q^N}{N!} \approx -N k_B T \left(\ln q - \ln N - 1 \right)$$

▶ Derive the chemical potential, μ,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \left(\ln q - \ln N - 1 + 1 \right) = -k_B T \ln \frac{q}{N}$$

▶ We will look at the pressure dependence of μ. Only the translational part of the partition function depends on the volume, so again $q = q_0 V$. Use the ideal gas law, $pV = N k_B T$,

$$\frac{q}{N} = \frac{q_0 V}{N} = \frac{q_0 k_B T}{p}$$

Ideal gas properties from quantum mechanics
Chemical potential, part 2

▶ $q_0 k_B T$ is denoted as the standard state pressure, p_{int}^o,

$$p_{\text{int}}^o = q_0 k_B T = k_B T \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} q_r q_v q_e \quad \Rightarrow \quad \mu = k_B T \ln \frac{p}{p_{\text{int}}^o}$$

where p_{int}^o represents an internal property of the molecule.

▶ Alternatively, in terms of the standard state chemical potential, μ_{int}^o (μ^o in the book),

$$\mu_{\text{int}}^o = -k_B T \ln p_{\text{int}}^o = -k_B T \ln(q_0 k_B T) \quad \Rightarrow \quad \mu = \mu_{\text{int}}^o + k_B T \ln p$$

▶ These three equations (in terms of q, p_{int}^o, and μ_{int}^o, respectively) for the chemical potential of an ideal gas will be used repeatedly in the forthcoming chapters.

Summary

- ▶ The molecular partition function was derived in terms of a translational, rotational, vibrational and electronic contribution.
- ▶ The quantum mechanical model systems (particle-in-a-box, rigid rotor and harmonic oscillator) were employed.
- ▶ The ideal gas was studied in detail. In particular, expressions for the chemical potential was derived.

E11.2. (Exam June 2011:2)

Molecular partition function

a) Give the partition function for an ideal gas with N indistinguishable molecules. Regard three types of systems: argon atoms, water molecules and butane (C_4H_{10}) molecules. Discuss the relative importance of the various contributions to the molecular partition function by comparing the three types of systems. The electronic ground state is not degenerate for any of of the systems. Which approximations do we do when we regard a gas as being ideal?

b) If we would like to calculate the pressure, p, from the partition function discussed in (a), which information is required about the molecules and about the system, respectively, to do the actual calculation?